William Marsh Rice University

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Covering

Research on the Physics of Solid Materials

For the Period

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Under the Direction

of

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and

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I. Introduction

Research in Materials Science and Solid State Physics and Chemistry at Rice University has been supported during the past eight and one-half years principally by National Aeronautics and Space Administration Grant NsG-6-59. The goals of the grant have been the following:

1.) To promote the growth and maturation of significant research in solid materials. Both basic and applied work has been supported. The distribution of funds is being made to those projects which appear to be most relevant to the objectives of NASA in the field of solid materials.

2.) To increase the competence of students and staff in the area of solid materials and to prepare Ph.D. students to assume responsible positions in materials research and development following their graduation.

3.) To increase interdisciplinary cooperation in fields related to solids so that students and staff may attain a broad competence instead of a narrow specialization.

To achieve the above goals, funds from this grant have been used to support research in areas involving workers from six University departments. As a consequence of this support, during this reporting period the accomplishments listed below were made possible.

1.) The program involved 16 faculty members, 28 graduate students and 6 post-doctoral fellows. The important research results obtained by these workers are described in Section II. A total of 21 publication references are given in Appendix I.

2.) The seminar program in solid materials organized last year for faculty and graduate students has been continued. The second year program (described below) was more successful than the first year one.

3.) A new course sequence in the physics of solids has been developed. This is an interdisciplinary sequence (described below) and gives the graduate students working in solid materials a broad and firm foundation for their work.

4.) Interdisciplinary cooperation is strong as a result of the associations made possible by increased utilization of the Space Science building for work on materials. Workers from four of the six University departments involved in materials research have space there.

The number of workers and level of publication is somewhat less than listed in the previous report. This is primarily due to the lower support level ($200,000/year) during the current grant year.

The research report given in Section II is a continuation of the format initiated with the last two progress reports. The research work on solids has been divided into five areas, and a status report written for each one by a single staff member in that area. These reports are written so that they may be of greater interest and use to the knowledgeable non-specialist. They attempt to place our work in perspective and show how it might contribute to a greater understanding and utilization of solid materials. These reports are still far from perfect, and our efforts to improve them will continue.

The interdisciplinary Solid State and Materials Science seminar instituted last year was continued. This was a weekly seminar whose participants represented all areas of research in materials science. In addition to the staff and graduate students, some outside speakers were presented. The topics of the initial seminars were:

1.) A Statistical Model of a Ternary Solid Solution
2.) Time Dependence of the Order Parameter in Dirty Superconductors
3.) Thermodynamics of Nonlinear Solids
4.) Paraelectricity: Resonance, Relaxation and Related Phenomena

This series has proved to be of great importance in stimulating interaction between the various research areas; efforts to improve it will continue.

A new interdisciplinary sequence of basic courses in the solid state is now in its first year of operation. Although not a new idea by any means, its institution at Rice is new, and a departure from past patterns. The sequence was made possible by the cooperation that resulted from the NASA supported Materials Science program. Descriptions of the five courses are given below.

1.) 563 - Introduction to the Solid-State

This course will provide an introduction to the fundamental concepts about crystalline solids, and provide the basic preparation for further courses in the sequence 564-567. It will consist of the following: a brief review of Quantum Mechanics and Statistical Mechanics, a discussion of crystal structure, a study of the diffraction of waves by lattices and an introduction to the concept of the reciprocal lattice, classical and quantum-mechanical descriptions of lattice vibrations and the thermal properties of insulators, and the properties of electrons in solids including free-electron and band-theoretical approaches. Prerequisites: An introductory background in wave mechanics and statistical mechanics, and concurrent enrollment in a graduate level quantum mechanics course is assumed.

Dr. Estle
Professor of Physics

2.) 564 - Electron Transport and Superconductivity

This course is one of the introductory graduate level courses on the solid state that follow 563. It will consider various aspects of electron transport, primarily from a microscopic viewpoint. Among topics to be covered will be various contributions to electron scattering and some techniques for measuring the Fermi Surface. In addition, an introduction to superconductivity will be presented. Prerequisite: 563 or equivalent.

Dr. Rudee, Assistant Professor
of Materials Science

3.) 565 - Dielectric and Optical Properties of Matter

This course is one of the introductory graduate level courses on the solid state that follow 563. Topics included are: polarization and the static model of a dielectric medium in an electric field; extension of the above model to the dynamic case and dielectric dispersion in solids; Raman and Brillouin scattering; optical spectra of solids; stimulated effects with applications to lasers; the dynamics of the nonlinear interactions between radiation and matter. Prerequisite: 563 or equivalent.

Dr. Rabson, Associate Professor
of Electrical Engineering

4.) 566 - Imperfections and Mechanical Properties

This course is one of the introductory graduate level courses on the solid state that follow 563. Point defects in crystals, geometrical description of dislocations and the mathematical theory of lattice imperfections will be discussed. Non-thermal generation of point defects, physical observation of defects in crystals and special properties of lattice imperfections in metallic, ionic and homopolar crystals will be covered. How lattice imperfections in ionic, metallic and homopolar crystals affect certain physical properties of these crystals will be developed. The effects of lattice defects, particularly dislocations, upon the mechanical properties of crystals will be discussed. Prerequisite: 563 or equivalent.

Drs. Roberts, Associate Professor
Materials Science &
Estle, Professor of Physics

5.) 567 - Magnetism and Magnetic Resonance

This course is one of the introductory graduate level courses on the solid state that follow 563. The basis of the magnetic properties of solids will be discussed. This will include diamagnetism, paramagnetism, ferromagnetism, antiferromagnetism, and ferrimagnetism. The phenomenon of magnetic resonance will be studied. This will include nuclear magnetic resonance, electron paramagnetic resonance, and ferromagnetic resonance. The emphasis will be on the atomic origin of magnetism and on a description of the elementary excitations of ordered magnetic materials. Prerequisite: 563 or equivalent.

Dr. Estle, Professor of Physics

A financial statement covering the period of this report is given in Appendix II.

A. Defect Structure and Mechanical Properties - F. R. Brotzen

Staff: F. R. Brotzen - Professor Materials Science
T. L. Estle - Professor of Physics
J. D. Ingram - Assistant Professor Mechanical Engineering
J. M. Roberts - Associate Professor of Materials Science
N. Soga - Assistant Professor of Space Science and Mechanical Engineering

Most investigations of defect structures and mechanical properties of solid materials carried out in the past under the sponsorship of this grant emphasized the study of lattice defects in metals and the relations between these defects and mechanical properties. Recently, however, through the addition of new projects a broader base for the research in this area has been found. As some of the investigators continue to study the relation between lattice defects and mechanical properties, others are concerned primarily with the description of isolated point defects in non-metallic crystals. Other researchers, in turn, approach the question of mechanical properties from a fundamental microscopic point of view. The pursuit of studies in these related fields by persons with varying backgrounds and diverse immediate aims is not only stimulating, but also promises to be especially fruitful as close cooperation between different investigators develops.

Microscopic studies of mechanical properties are conducted both theoretically and experimentally.

1. Waves in Non-Linear Materials.

The objective of this theoretical project is to establish, through analysis of wave propigation data, the relations between non-linear phenomenological coefficients in the macroscopic theory of the response of materials. It has been possible to develop a method for the conversion of the non-linear partial differential equation of the form

$$\frac{\partial^2 u}{\partial x^2} + \frac{\varepsilon \partial u}{\partial x} \frac{\partial^2 u}{\partial x^2} = \frac{\partial^2 u}{\partial t^2}$$

to an integral equation which is soluble by iteration techniques. The method used consists of a combination of Laplace and Fourier transform methods with the theory of generalized functions. An analogous method is now being used on the non-linear partial differential equations of elasticity. This procedure places all of the coupling between compressional and shear motion in the integral terms and will provide an immediate analysis of the non-linear effects. The method described above will be applied to various specific forms of constitutive equations and compared with experimental data.

2. Sound-Wave Velocities and Elastic Constants of Solids. The aim of this program is to determine the sound wave velocities and elastic constants of inorganic compounds at high pressures and low temperatures and thereby to obtain their equations of state. Construction of an ultrasonic-interferometer system for measuring sound-wave velocities of solids and of a 2 kilobar nitrogen compression system was begun when this project started in May, 1967. This system was completed in October, 1967, with the partial aid of the NASA Sustaining Grant NGR 44-006-033. A study was carried out to determine the behavior of sound velocities of σ-quartz under varying pressures and temperatures. Analysis of the data shows that the shear velocity behaves anomalously with pressure. A working hypotheses to explain this observation considers a pressure-induced shear instability, which occurs before actual phase transformation takes place. This hypotheses can be checked by measurements on other compounds. In addition to their fundamental interest, the pressure and temperature derivatives of the sound velocities of quartz are also important for the study of the interior of the earth, because silicon dioxide is one of the major constituents of the earth's crust and mantle. Measurements of elastic constants of calcium oxide and beryllium oxide under pressure will be undertaken in the near future.

The study of imperfections in the lattice of metallic crystals is of particular importance because mechanical properties are directly relatable to the defect structures. Several projects are presently underway that center about the study of this relationship:

3. Dislocation Mechanisms in Body-Centered Cubic Metal Crystals.

It is the purpose of this program to study the effect of external variables, such as temperature, stress, strain, strain rate, and impurity content on the motion and distribution of dislocations in body-centered cubic crystals, notably in molybdenum. It is well known that metals and alloys possessing a body-centered cubic structure are highly temperature and strain-rate sensitive as far as their strength and ductility are concerned. A basic understanding of the mechanisms that underlie plastic deformation in these materials is of particular importance because some of the most important metallic structural materials, such as steel, have a body-centered cubic structure. The present phase of this investigation centers about the properties of molybdenum which also crystallizes in the body-centered cubic system and which can be produced in single-crystal form with a high degree of purity. Most of the work during the past six months was devoted to a study of molybdenum-rhenium alloys, since it is known that the addition of rhenium changes drastically the plastic behavior of pure molybdenum. It has been suggested that additions of rhenium change the stacking fault energy. This, in turn, produces an alteration of the atomic arrangements within dislocations (the defect that produces plastic deformation). Since the addition of rhenium to molybdenum also changes the electronic structure, this phase of the program promises to contribute to the general knowledge of the relation between alloying theory and deformation mechanisms. Since it is conceivable that the addition of rhenium to molybdenum would alter not only the stacking-fault energy, but also the elastic constants, a study of the latter was begun. The adiabatic elastic constants of molybdenum, as well as alloys containing 8, 15, and 25 at. % rhenium, were determined over a temperature range from 78°K to about 400°K. Material of the desired nominal compositions was obtained in the sintered condition from the Chase Brass Company. The bars were subsequently hot swaged into ¼" and 1/8" rounds. Since it was desirable to make the determination of the elastic constants in bars of ¼" diameter, special equipment for growing single crystals had to be designed and built. Measurement of the elastic constants requires a preliminary investigation of the thermal expansion coefficients. After this was completed, the adiabatic elastic constants of the three alloys were determined as a function of temperature by the pulse-echo method. The ultrasonic interferometer system described in (2) above was used successfully in determining the elastic constants of the molybdenum-rhenium alloys. The results reveal that the elastic constant c_{44} increases substantially with the addition of rhenium to the molybdenum. The same is true for the elastic constant c_{12}. It is interesting to note that molybdenum, which is not elastically isotropic in the pure condition, becomes an isotropic material at approximately 27% rhenium.

4. Microstrain, Microcreep, and Amplitude-Dependent Dislocation Damping in Metal Crystals.

The immediate objective of this research is to study how different statistical distribution functions of dislocation loop-lengths affect the amplitude-dependent internal friction and to correlate the results with experimental data. These studies of the hysteresis loss due to the breakdown of attractive dislocation junctions for various loop-length distributions revealed that only the Gaussian distribution agrees with the data for copper crystals, and even here the agreement is only fair. Examination of the Gaussian distribution over a wide range of variables is now just being completed and is being put in manuscript form.

An examination of the basic rate equation for the macroscopic strain rate is also being undertaken. A computer program has been formulated to analyze this equation. The stress dependence of the various parameters in the equation are investigated for dislocations interacting with either rigid or nonrigid barriers. The experimental program to study stress relaxation in tantalum and tantalum-rhenium single crystals has proceeded to the stage where about 100 tantalum crystals have been made with an orientation such that the maximum resolved shear stress is on a $(1\bar{1}0)$- 111 slip system. The alloy crystals are also in preparation and will be grown in the electron-beam melting apparatus by attaching a rhenium wire to the tantalum rod and melting them together. The rhenium content has been varied from 2.5 to 12.5 weight percent by this technique in one beam pass. For the stress relaxation study of molybdenum single crystals, the measurement of the ratio of $(\sigma_f/\sigma_r)_{\varepsilon p}$ as a function of T is now almost complete. Here σ_f is the flow stress and σ_r is the completely relaxed stress at constant plastic strain. This ratio should be approximately independent of temperature if σ_r is related to the structural stress τ_g. If so, the results will yield an independent confirmation of the microcreep results of Herring, Brotzen, and Roberts.

5. The study of isolated point imperfections in nonmetallic crystals includes an extensive program concerned with spectroscopic studies of point imperfections. The objectives of this research project are to obtain detailed atomic-scale descriptions of isolated point imperfections in nonmetallic crystals and of their lower-energy states. In order to accomplish this, it is necessary to have numerous precise data of the sort which usually result from spectroscopic studies. This gives a quantum-mechanical picture of the lower-energy states from which one can infer much about the imperfections with considerably higher reliability than is customary in most studies of imperfections and their properties.
This project was begun June 1, 1967. The first phase was to use the microwave spectroscopic technique of paraelectric resonance to study electric dipoles in solids. There are several ways by which imperfections can have electric-dipole moments in crystals. One of these is for the imperfection to be an impurity molecule which itself has an electric dipole moment. Frequently these dipoles will find several orientations in the crystal which are otherwise equivalent and will occupy all of these orientations with equal probability. Applying an electric field to the crystal causes the energies of the variously-oriented dipoles to differ. If the temperature is low enough this should result in a net polarization of the

dipoles, provided that the time required for a dipole to change its orientation is short enough. This time is frequently controlled by a process in which the dipole absorbs sufficient energy from the thermal vibrations in the crystal so that it passes over the energy barrier separating the minimum-energy orientations. At low temperatures, no "transitions" between the different orientations are possible for such a process and no polarization occurs. However, quantum mechanics allows the dipole to tunnel through the barrier so that for a sufficiently small barrier one may find that the "transitions" occur rapidly. Not only can this lead to large polarization at low temperatures and large electric fields, but it also leads to a completely new phenomenon: paraelectric resonance. Paraelectric resonance is the electric analog of paramagnetic resonance and results from electric dipole transitions between the states of the system arising from tunneling and the effect of the electric field on the different orientations of the dipole. Future plans include a detailed comparison of experiment to theory. This has not been done yet, and the theory has only appeared in small part in the literature. A complete theory has been developed by Dr. Estle at Rice. A search will also be made for narrow resonance lines. All results reported to date are concerned with broad lines having a width comparable to the position. The work will be carried out over a wide range of materials, since all research so far has been on KCl and a few other alkali halides. Eventually, a study of the effects of uniaxial stress and of simultaneous paramagnetism will be carried out. The possibilities of paraelastic resonance will be explored.

B. Electrical and Optical Properties - H. E. Rorschach

Staff: L. E. Davis, Assistant Professor of Electrical Engineering
R. B. McLellan, Assistant Professor of Mechanical Engineering
T. A. Rabson, Associate Professor of Electrical Engineering
H. E. Rorschach, Professor of Physics
M. L. Rudee, Assistant Professor of Materials Science
G. T. Trammell, Professor of Physics

Research on the electrical properties of matter is of fundamental importance for an understanding of the electronic structure of solids and their interaction with electromagnetic waves of all frequencies. This understanding, in turn, is necessary to provide a foundation for the application of solid state phenomena to new electronic devices. Investigators in materials research at Rice are studying the electromagnetic properties of solids at frequencies from zero (static fields) to those associated with Mössbauer gamma rays.

1. Static Properties

Work by Professors Dessler and Michel in the Space Science department and Rorschach and Trammell in the Physics department on the gravitationally induced electric field in metals has been completed and accepted for publication. This work has been the center of a controversy involving the interpretation of an experiment by F. Witteborn and W. Fairbank at Stanford on the "free fall" of an electron. To measure the influence of gravity on a free electron requires careful shielding of all stray electric fields. A careful study of the electric field generated by gravity acting on the shield itself is also required, and this study was initiated by Schiff and Barnhill at Stanford. Their calculation (published in the Physical

Review, 161, 1067, 1966) showed that an electric field of 10^{-11} volts/meter would be produced near the shield, due to the "sagging" of the electrons in the shielding material. Their calculation neglected the influence of gravity on the positive ions in the material, and this omission was corrected in the work of the Rice group, who made a self-consistent calculation of the field due to the action of gravity on both the electrons and the positive ions in the shield. This calculation gives an electric field of 10^{-6} volts/meter in a direction opposite to that of the field of Schiff and Barnhill. The Rice group has now received support for their results from other investigators and this work has stimulated a re-examination of the experiments, which had originally appeared to support the conclusions of Schiff and Barnhill. It now seems clear that a correct application of the principles of solid state physics predicts a field of the order of 10^{-6} volts/meter; the considerably smaller field observed in the Stanford experiment requires some new feature, not included in any theory yet proposed.

2. Microwave Properties

Improved techniques for the production of electromagnetic waves in the millimeter wave-length range are leading to increased use of these wave-lengths in spectroscopy, prototype radars and communication systems. The development of nonreciprocal devices that is, devices such as circulators in which the wave is affected differently for different directions of propigation, is necessary if this wavelength range is to be useful. The suggestion has been made that a semi-conducting material of properly adjusted electron density would be a more useful nonreciprocal medium than ferrites in this frequency range. Some theoretical work has now been started at Rice to investigate the feasibility of such devices. Calculations have been made for a model consisting of a plasma subjected to a uniform magnetic field. The propagation of electromagnetic waves in this medium shows the required transition from reciprocal to nonreciprocal waves as the magnetic field and density are varied. Experimental work will be needed to assess fully the value of semi-conductors as nonreciprocal media, since Fermi surface effects not present in the plasma will play an important role.

3. Optical Properties

Coherent optical sources (lasers) are becoming of increasing technical importance. They are essential in the development of new information storage and presentation methods based on optical holography. Focused lasers are also finding use as high density energy sources for ionization of gases and solids. The properties of laser light are being studied by Professor Rabson. High time resolution techniques have been used to study the characteristics of the short-duration spikes that make up a burst of laser radiation. It had previously been thought that these burst were unpolarized. Examination of the individual spikes at normal power levels showed that they were each fully polarized but uncorrelated in polarization with neighboring spikes. At low power levels, correlation between spikes appears, and the polarization is related to the crystalline axes of the laser rod. The influence of an external magnetic field is presently being investigated. Application of transverse fields as high as 28,000 Gauss is now possible, and studies of the influence of Zeeman splittings on the characteristics of the emitted light should give new insight on the polarization effects. To facilitate interpretation of these experiments, a theoretical description of the polarization properties has been developed which makes use of the analogy between photons and massless spin-one particles. A density matrix representation for this case is being applied to the problem of optical pumping in the presence of a magnetic field.

The high resolution techniques developed for polarization studies are now being extended to study the time coherence of radiation from various sources, including lasers.

The use of a laser as a high density energy source is being investigated in connection with the analysis of surface composition by means of a mass spectrometer. The surface can be vaporized by a focused laser beam. An optical system has been developed to transmit the laser beam to a sample surface inside a mass spectrometer. The system will be used initially for a study of the surface composition of crystals of silicon, germanium and gallium arsenide.

4. Gamma Ray Properties

Transitions between low-lying nuclear states of long life are responsible for the emission and absorption of gamma rays of sharp energy. In addition, if the recoil momentum is taken up by the entire crystal, there will be no shift in the frequency of the emitted radiation (Mössbauer effect). The utilization of Mössbauer absorption has become an important experimental technique for the study of solids. The chemical environment of the resonant nuclei and the magnitude of local magnetic fields can be determined with this method. The use of Mössbauer gamma rays for diffraction (scattering) studies has received little attention. Professor Trammell has developed a quantum theory for the propagation and diffraction of these gamma rays which is now being published in a series of papers in the Physical Review. The first paper, on the fundamental theory, has appeared, and succeeding papers will discuss the application of the phenomenon of resonant scattering to structure determinations.

Professors McLellan and Rudee have been making use of the properties of Mössbauer radiation to study the phonon spectrum of solid solutions. A vibrating atom will emit Mössbauer radiation shifted in frequency because of the relativistic time dilation associated with its motion (2nd order Doppler shift). This frequency shift for the iron solute nucleus can be related to the vibrational frequency of the mode associated with that atom. Solid solutions of iron in platinum are presently being studied.

Preliminary results were unsatisfactory because of an inadequate Mössbauer drive mechanism. It is being replaced with a high precision drive.

Professor Trammell has also been studying the fundamental theory of microscopy based on waves of short-wavelength (gamma rays, neutrons, electrons). There have been various proposals to examine single molecules by the use of gamma ray holography. Prof. Trammell and his students have shown that this idea is worthless, since the cross section for the production of photo electrons is so large that gamma-ray observation of the molecule would destroy it. A similar result holds for neutrons, and electron microscopy appears to be the most promising method. The elastic electron-atom cross section is large compared to the inelastic cross-sections. Even here, however, there is a serious question that is presently being studied of whether or not the radiation damage will alter the molecule.

C. Magnetism andSuperconductivity - H. E. Rorschach

Staff: H. C. Bourne, Professor of Electrical Engineering
P. L. Donoho, Professor of Physics
W. V. Houston, Professor of Physics
H. E. Rorschach, Professor of Physics
G. T. Trammell, Professor of Physics

Research in this field is concerned with the magnetic properties of rare earth metals and with time dependent and dissipative processes in superconductors.

1. Magnetic Properties of the Rare Earth Metals

The magnetic properties of the rare-earth metals are in many ways strikingly different from those of the more common magnetic materials, such as the elements of the iron group and their alloys. The principal reason for these differences lies in the fact that the rare-earth ions in a metal possess highly localized magnetic moments, in contrast to the iron-group metals wherein the magnetic moments are carried by the conduction electrons and are therefore distributed throughout space much more uniformly than those of the rare earths. Because the magnetic moments of the rare-earth ions are highly localized, the magnetic properties of the metals are strongly dependent on the nature of the symmetry of the fields acting on the electrons of the rare-earth ions. For this reason, the magnetic properties are highly anisotropic, reflecting the hexagonal symmetry of the crystal. The role played by the anisotropy is not fully understood, but it certainly gives rise to highly anisotropic terms in the Hamiltonian of the crystal, and results, in the case of dysprosium and other elements, in strong preferential alignment of the magnetization. Furthermore, the localized nature of the f-electrons, which give rise to the magnetic properties, necessitates an indirect type of exchange interaction, which under certain circumstances gives rise to a very complicated arrangement of the magnetic moments of the individual ions. For example, peculiar antiferromagnetic helicoidal and cycloidal moment structures can occur in certain temperature ranges for nearly all the rare earths in the last half of the lanthanide series.

The purpose of the work being carried out at Rice is to try to understand the excitations of the system of magnetic moments from their equilibrium state by studying the response of various quantities to stimulation by system. By adjusting the flow-rate of the helium gas and by using a sensitive temperature sensor together with a high-gain feedback-control system it is possible to obtain a regulated temperature within $\pm$ 20 millidegrees at any temperature within the desired range. A paper is being prepared for publication describing the construction and operation of this cryostat, which represents a significant contribution to the field of microwave spectroscopy at variable temperatures in the cryogenic range.

The experimental measurements obtained to date have been of three main types, which are discussed separately in what follows. Although the results are not fully understood as yet, they represent the first reproducible microwave absorption measurements on dysprosium, and when interpreted by means of a theoretical analysis, they will undoubtedly shed light upon the nature of the desired properties, principally upon the nature of the magneto-elastic interaction.

a. Non-resonant Absorption:

There is a strong absorption dependent upon magnetic field strength and upon temperature. This absorption undergoes a rapid change with increasing magnetic field at a field value known as the critical field. This critical field is well known from other types of measurement, and is the value at which the field causes a collapse of the antiferromagnetic helicoidal spin structure into a ferromagnetic structure. An analysis of this absorption assuming an instantaneous response of the magnetic moments to a rapidly varying magnetic field is in good agreement with the results. However, this effect does not reveal as yet a great deal about the properties of interest, although when the theory is refined somewhat, the role played by magnetoelastic interactions in this nonresonant absorption should become clear. Work on the theory is in progress.

b. Resonant Critical Field Absorption:

From the point of view of the theoretician, the strong resonant absorption observed at the critical field is of the greatest importance. This resonance was only discovered through a very careful search of the dependence of the absorption on the direction of the magnetic field. It is only found when the crystal is in the antiferromagnetic temperature range, and only when the field is aligned along what would be the direction of easy magnetization in the ferromagnetic range. Such a resonance was predicted earlier, but the prediction indicated that its dependence on magnetic field direction would be negligible. Obviously the anisotropy energy is playing a very important part here, and a theoretical investigation is in progress to determine the resonant properties of the magnetic system taking anisotropy into account properly. The width of the resonance is governed by magnetoelastic properties, and the theory takes these properties into account also.

c. Resonant Hexagonal-Anisotropy Absorption:

In the ferromagnetic region, there is a strong anisotropy which keeps the magnetic moments aligned along the so-called easy direction in the basal plane of the hexagonal crystal structure. This anisotropy is such that an applied magnetic field along the so-called hard direction of magnetization can produce a situation in which a sort of ferromagnetic resonance can occur in the microwave frequency range. This resonance, which has been observed, should have two peaks. If one applies the accepted theory which predicts this resonance, it is possible to deduce the nature and magnitude of the so-called hexagonal-anisotropy energy. When this calculation is made, however, the results disagree strongly from those found by other accepted methods. It is felt that this disagreement is due in some way to the strong magnetoelastic interaction which distorts the crystal substantially from its normally hexagonal shape to an orthorhombic structure. Theoretical investigations are in progress to try to understand this problem.

Future work in this area includes the development of the theory of microwave absorption in dysprosium to the degree necessary to explain the observed phenomena. The theoretical calculations require, however, the numerical solution of problems which involve the diagonalization of 26th order matrices, and the investigation right now is concerned with programming the calculations for a high-speed computer. Experimental work will include further studies of holmium, gadolinium, and terbium. Also, because of the enormous magnetostriction which these elements exhibit, work is in progress to construct a microwave ultrasonic transducer, which promises to have a higher efficiency than any presently known transducer by at least two orders of magnitude.

Professor Trammell has been investigating the theory of magnetic ordering in the rare-earth metals. The spin coupling of the rare earth ions is indirect, being caused by their direct coupling to the conduction electrons. It had previously been assumed that this coupling was nearly isotropic; i.e., that the coupling was dependent on the angle between the spins of two ions, but largely independent of the angle that the spins made with the line joining the two ions. As reported previously, Dr. Specht at Rice made a theoretical investigation which indicated that there should be a large anisotropic contribution (of the order of 50%) to the spin-spin coupling. Dr. Specht's paper has now appeared in the Physical Review. Inasmuch as the magnetism of the rare earths is a field of great current interest and activity, and since the spin-spin coupling is fundamental in determining the magnetic behavior of materials, these theoretical results are of considerable interest. Inelastic neutron diffraction data on the rare earth metals are currently becoming available. The analysis of these data should determine the magnitude of these anisotropic exchange effects.

2. Superconductivity

Theoretical and experimental studies of the dissipative effects that can occur in the superconducting state due to the trapping, motion, and expulsion of magnetic flux have been undertaken. The technological interest in this work is due to ideas concerning the possibility of efficient high energy transmission lines built of superconductors carrying high currents at low voltage instead of the present high tension transmission lines. It is also of interest in connection with the present construction of superconducting linear accelerators to reduce the large resistive energy losses and to increase their short duty cycle. It is of interest, in principle, in identifying the energy losses which must occur in the various superconducting devices proposed for electric generators and control purposes.

Dr. Houston and his students have completed work on energy losses associated with the motion of magnetic flux in indium, a "Type I" superconductor. This work has now appeared in the Physical Review. The dissipation due to motion of a localized "flux spot" through plates of varying thickness was investigated. The results have been interpreted in terms of a recent theory of viscous flux motion due to J. Bardeen and M. Stephen. (Phys. Rev. A140,1197 (1965)) The losses in niobium (a "Type II" material) under similar conditions are presently being studied.

Experiments on the A. C. losses in Nb-Zr superconductors have been described in previous reports. This work is now complete and has been published in Applied Physics Letters. The magnetization curves and resistive losses in Nb-Zr wires have been measured as a function of the alternating current flowing in the wire sample. The influence of a longitudinal magnetic field on the losses has been studied, and it was shown that such fields can substantially reduce the losses and increase the A. C. critical current.

Dr. Rorschach and his students have studied the trapping and expulsion of magnetic flux in molybdenum. This material is a superconductor with a low transition temperature (T_c=0.9^{o}K).

At temperatures below $0.9^{O}K$, the usual Meissner effect (flux expulsion) is modified due to phenomena associated with the transfer of heat from the sample to the cooling bath of liquid helium 3. The object of this research is to study the dynamics of the flux trapping and the time dependent effects associated with its escape in zone refined single crystals of high purity. A helium-3 cryostat has been used to obtain quite accurate data on the thermodynamic properties of superconducting Mo. The nature of the phase-transition (form of the trapped flux and its rate of escape) has been studied as a function of the rate of variation of the external field. A good picture of the way superconductivity is destroyed has been found, but an adequate picture of the way the superconducting state is established and the mechanism of flux trapping is still lacking. The flux trapping observed in Mo is novel for this type superconductor. Measurements are in progress to try to understand the form in which flux is trapped and its mechanism of escape as the external field is reduced. Additional specimens of Mo, as well as other superconductors, will be investigated.

The theoretical understanding of dissipative effects has been based mostly on rather crude models. The phenomenological description of superconductivity is based on the "Ginsburg-Landau equations." These equations describe the electrodynamic properties (principally magnetic effects) and are in some sense simplifications of the complicated microscopic equations and thus more suitable for engineering applications. The modification of these equations so that they describe time-dependent effects (flux flow, dissipation, etc.) and the application to some simple practical cases are the objectives of some theoretical work being undertaken by Dr. Young, a research associate at Rice. The microscopic theory of superconductivity has been used to derive an appropriate form of the Ginsburg-Landau equations. The usual form of these equations has been modified so that they are valid over a wider range of temperatures and so that time dependent effects may be treated. The modified equations will be used to study some important time-varying effects, such as flux-flow (motion of vortex lines in a superconductor). It is possible that they may be used also to treat other transport properties.

D. Thermodynamics and Solid Surfaces - R. Kobayashi

Staff: R. Kobayashi, Professor of Chemical Engineering
J. L. Margrave, Professor of Chemistry
R. B. McLellan, Assistant Professor of Mechanical Engr.
T. A. Rabson, Associate Professor of Electrical Engr.

1. Thermodynamic and Transport Measurements on Solids

Professor McLellan and his students have studied the properties of solid solutions. The work is designed to obtain experimental values for the thermodynamic parameters of solute atoms in dilute solid solutions which can be compared with the predictions of various theoretical models.

A theoretical model for dilute ternary solid solutions has been devised. This is a statistical model which explains the thermodynamic behavior of these solutions in terms of given interaction energies. Thus it can be regarded as being an extension of a whole body of previous statistical interaction theories which have been applied in the past to binary solid solutions. Thermodynamic data for iron-base solid solutions containing transition metal solutes substitutionally and carbon interstitially have been analyzed in the light of this model. Very good agreement has been obtained.

Apparatus has been built to measure the temperature dependence of the equilibrium between iron-carbon solid solutions and mixtures of H_2 and CH_4. The analysis of the results will yield the entropy and energy of a carbon atom. The energy is of fundamental importance, since it is the simplest thermodynamic parameter of the complex Fe-C system and has been a center of doubt for the last decade. Measurements have also been made of the temperature variation of the C-solubility of cobalt, nickel, platinum and palladium. The vibrational entropies of the C-atoms in these solutions have been found and the results compared to theoretical models. Theoretical work has also been done on refined models for interstitial solutions.

Progress has been made on a mass flow apparatus for determining the diffusivity of interstitial elements in B.C.C. metals. The data are vitally important in view of the recent findings of the anomalous diffusivity of carbon in B.C.C. iron and chromium. Some previous data are available but they are mainly from elastic measurements and are very much open to question.

Professor Kobayashi has continued the work on gas hydrates which was described in previous progress reports. Apparatus for the measurement of the occupation numbers of methane and ethane in their respective hydrates has been completed and preliminary results obtained. The measured occupation numbers have been compared with statistical mechanical calculations and good agreement has been found.

2. Interactions Between Gases and Solid Surfaces and the Structure of Solid Surfaces

Professor Margrave's work on reaction mechanisms has continued to yield new chemical compounds. The Bendix time-of-flight and mass spectrometer have been applied to studies of the rates and mechanisms by which gaseous molecules interact with solid surfaces in processes such as sublimation, vaporization and corrosion, over wide ranges of temperatures and pressures. Studies have been completed on several fluorides, oxyflourides, chlorides, oxides and sulfides. New gaseous compounds discovered were $LiCoO_2$, $LiNiO_2$, LiGaO, and LiInO.

Two new programs are under development. A time-resolved mass spectrometer for kinetic studies (e.g. reaction rates) has been designed and constructed. The study of high-pressure phases, such as the borides of tin, cadmium and the alkali metals, has been initiated and will be expanded during the next few months.

Work with Professor Rabson on the mass spectrometric studies of laser vaporized surfaces is continuing. (See section B)

Professor Kobayashi and his students have continued their development of perturbation gas chromatography for use in the investigation of gas-surface interactions (adsorption phenomenon). A new notion has been developed, that of the "hypothetical perfect gas perturbation," in which a series of perturbations (e.g. helium, neon, argon, etc.) is made in a chromatographic column to measure its free gas volume by energy extrapolation of the retention times or volumes to zero energy of interaction. This notion has been combined with experimental retention volume data to obtain several results:

a. Accurate absolute and Gibbs adsorption isotherms have been measured for gases and their mixtures.

b. The volume of the adsorbed phase has been determined.

c. The conditions, under which identity of gas-solid and gas-liquid equilibrium obtains between non-polar gases and sintered glass beads, have been determined.

d. The interaction between unlike non-polar molecules adsorbed on sintered glass beads (polar surface) has been investigated and shown to lead to non-ideal mixture behavior.

E. Thin-Film Properties - H. C. Bourne, Jr.

Staff: H. C. Bourne, Jr., Professor of Electrical Engineering
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Vacuum-evaporated magnetic films of thicknesses ranging from several hundred to several thousand angstroms and widths of the order of 1 cm have several interesting properties that suggest possible applications as computer memory or logic elements and as parametric device elements. In addition these thin films provide an almost unique vehicle for studying many magnetic phenomena not completely understood.

When these films are deposited in the presence of a magnetic field or at oblique incidence and when the composition is nominally 80-20 Ni-Fe (nonmagnetostrictive), they exhibit a uniaxial anisotropy (the films exhibit an easy direction of magnetization). The energy involved is of such a magnitude that an externally applied field of 2 to 5 oersteds is necessary in order to rotate the magnetization in the hard direction. In addition, under sufficiently large switching fields and appropriate bias fields these films may be switched from one easy direction to another in a time of the order of 1 nanosecond. These characteristics are certainly of interest in the applications mentioned.

Two basic aspects are in need of clarification. The exact origin of the uniaxial anisotropy is not completely known, and consequently the magnitude, the dispersion in magnitude, and the dispersion in angle are not easily controlled. Further these films usually switch by much slower processes than the single domain rotation of 1 nanosecond duration described above. The overall research goal of this program is to understand the static and dynamic switching properties of these films sufficiently well that these properties may be controlled by structural and drive modifications and that their usefulness in important applications will be greatly enhanced.

To this end, three important mechanisms of flux reversal associated with the propagation of domain boundaries have been identified. The first mechanism consists of the growth of relatively few domain tips parallel to the easy axis followed by the broadening of these stripe domains by transverse wall motion. The second mechanism occurs when the domain tips form two continuous zig-zag walls which, moving longitudinally parallel to the easy axis, almost completely switch the film. The process proceeds with velocities and mobilities an order of magnitude greater than the classic wall motion process. A third process is still another order of magnitude faster and proceeds by the movement of a very fine-structured domain boundary in the same manner as the zig-zag wall. The switching times involved are those associated with the incoherent region, and, although the boundary may be just a fine-structured zig-zag wall, the reason for the order of magnitude increase in speed is not understood. These mechanisms probably dominate in most practical thin film devices.

The behavior of thin film magnetization has been studied under the action of a hard-axis pulse field. Under appropriate conditions this excitation results in total demagnetization of the film and a further oscillatory motion. This behavior is very detrimental to proper memory operation. Experimental data have been obtained preparatory to constructing a model which may give some clue to appropriate means of suppressing these phenomena.

A second vacuum evaporation system has been put into operation which permits the rapid fabrication of thin films under varied conditions. Films have been deposited at temperatures ranging from $77^{\circ}K$ to $400^{\circ}C$ in order to initiate new studies of annealing effects on anisotropy, dispersion, and coercive force using the sensitive torque magnetometer.

In addition, during this period, the capabilities for magnetic measurements have been extended by modifications which allow the anisotropy field, coercive force, and magnetic thickness of the films to be measured more accurately. In addition, the angular dispersion of magnetization about the easy axis can now be quantitatively determined.

A concerted effort is in progress to measure the structural properties of permalloy films prepared by the "boat evaporation" technique and to relate these properties to variations in the evaporation conditions. The technique involves the melting and evaporation of a small quantity of permalloy from a large resistance heated tungsten boat; the evaporant is subsequently condensed onto glass substrates to form thin films. Very high deposition rates are obtained, often in excess of 2000Å/sec.; a very fine grain size is caused by the high evaporation rates. Film thickness and average composition were found to be controlled by the kinetics of melting, wetting, and alloying of the charge with the boat and by deviations from Raoultian vapor pressures of Ni and Fe. Concentration gradients through the film thickness have been found as well, and are also the result of alloying and vapor pressure conditions. A semi-quantitative theoretical description of these observations has been developed.

APPENDIX I

Publications During the Period of this Report

A. Defect Structure and Mechanical Behavior

1. L. D. Whitmire and F. R Brotzen
"Effects of Impurities on the Plastic Flow of Molybdenum Crystals."
Accepted for publication in the Proceedings of the International Conference on the Strength of Metals and Alloys, Tokyo, Japan, 1967.

2. J. M. Roberts
"Relaxational Dislocation Damping Due to Dislocation-Dislocation Intersections with Application to Magnesium Single Crystals." Accepted for publication in the Proceedings of the International Conference on theStrength of Metals and Alloys, Tokyo, Japan, 1967.

3. M. Yabe and J. M. Roberts
"A Rapid and Accurate System for the Measurement of Ultrasonic Attenuation by the Pulse Method."
Accepted for publication in the Review of Scientific Instruments, January, 1968.

4. N. Soga
"The Temperature and Pressure Derivatives of Isotropic Sound Velocities of σ-Quartz." Accepted for publication in J. Geophy. Research, January, 1968.

B. Electrical and Optical Properties

1. A. J. Dessler, F. C. Michel, H. E. Rorschach, and G. T. Trammell
"Gravitationally Induced Electric Fields in Conductors."
Accepted for publication in Phys. Rev., April, 1968.

2. J. P. Hannon and G. T. Trammell
"Mössbauer Diffraction I: Quantum Theory of Gamma-Ray and X-Ray Optics." Accepted for publication in Phys. Rev.

C. Magnetism and Superconductivity

1. F. Specht
"Indirect Exchange Effects in the Rare Earth Metals."
Phys. Rev., 162, No. 2, pp. 389-398, 10 October 1967.

2. W. V. Houston and D. R. Smith, "Motion of Magnetic Flux Through Superconducting Strips," Phys. Rev., 163, No. 2, pp. 431-434, 10 November 1967.

3. Henry F. Taylor, "Alternating-Current-Induced Voltages in Superconducting Wires," Phys. Rev., 165, No.2, pp. 517-521, 10 January 1968.

4. Henry F. Taylor, "Studies of Superconducting Nb-25% Zr Wires Carrying Alternating Current in an Axially Applied Magnetic Field," Applied Phys. Letters, 11, No. 5, 1 September 1967.

D. Thermodynamics and Solid Surfaces

1. K. Zmbov and J. L. Margrave, "Mass Spectrometric Study at High Temperatures. XXII. The Stabilities of Tantalum Pentafluoride and Tantalum Oxytrifluoride," Accepted for publication, J. Phys. Chem., (1968).

2. J. W. Hastie, K. F. Zmbov and J. L. Margrave, "Mass Spectrometric Studies at High Temperatures. XXIII. Mass Spectrometric Studies of Vapor Equilibria Over Molten $NaSnF_3$ and $KSnF_3$," Accepted for Publication, J. Inorg. Nucl. Chem., 1968.

3. J.W.Hastie, P. Ficalora and J. L. Margrave, "Mass Spectrometric Studies at High Temperatures. XXV. Vapor Composition of $LaCl_3$, $EuCl_3$, and $LuCl_3$ and the Stabilities of the Trichloride Dimers," Accepted for publication, J. Less Common Metals, (1967).

4. P. Ficalora, J. C. Thompson and J. L. Margrave, "Mass Spectrometric Studies at High Temperatures. XXVI. The Sublimation of SeO_2 and SeO_3," accepted for publication, J. Inorg. Nucl. Chem., (1967).

5. K. F. Zmbov and J. L. Margrave, "Mass Spectrometric Studies at High Temperatures.XXIV. Sublimation Pressures for TiF_3 and the Stabilities of $TiF_2(g)$." Accepted for publication, J. Phys. Chem., 71, 2893 (1967).

6. K. F. Zmbov and J. L. Margrave, "Mass Spectometric Studies at High Temperatures. XXI. The Heat of Atomization of Gaseous Oxyfluoride," Accepted for publication, J. Inorg. Nucl. Chem. 29, 2649 (1967).

7. S. Masukawa and Riki Kobayashi, "The Hypothetical Perfect Gas Perturbation and the Determination of the Volume of the Adsorbed Phase in Gas-Solid Chromatographic Columns," to be published, The Journal of Gas Chromatography, October 23, 1967.

8. S. Masukawa and Riki Kobayashi, "Adsorption Equilibrium of the System Methane-Ethane-Silica Gel at High Pressures and Ambient Temperatures," to be published, The Journal of Chemical and Engineering Data, December 1, 1967.

9. J. Sprague and Rex B. McLellan, "Iron-Carbon Solid Solutions," accepted for publication AIME TRANS., (1968).

10. J. Sprague and Rex B. McLellan, "The Fe-C Austenite Solid Solution," accepted for publication AIME TRANS.,

E. Thin Film Properties

1. K. R. Carson and M. L. Rudee, "An Improved Specimen for Alignment of Electron Microscopes," J. Sci. Instrum., 44, 1036 (1967).